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Pseudomorphic Stabilization of Diamond on Non-Diamond Substrates: Heteroepitaxially Grown Diamond on a c-BN {111} Surface

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HETEROEPITAXIALLY GROWN DIAMOND ON A c-BN {111} SURFACE

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ABSTRACT

A continuous diamond film with a thickness of about 10 microns was grown on {111} faces of single crystal cubic boron nitride (c-BN) by hot-filament chemical vapor deposition (CVD). The morphology and microstructure of the diamond film were investigated by scanning and transmission electron microscopy. Cross-sectional selected area diffraction pattern (SADP) and high resolution electron microscopy (HREM) of the diamond/c-BN interface show that the diamond has a parallel orientation relationship with respect to the substrate. Indirect evidence from scanning electron microscopy indicates that parallel epitaxy was achieved over the entire boron terminated face of the c-BN crystal, which had linear dimensions of approximately 400 microns.

Heteroepitaxial growth of diamond on foreign substrates has great potential scientific and technological importance. If diamond films with low defect densities can be grown, many advanced electronic devices can be fabricated[1]. Cubic boron nitride (c-BN) is one of the most promising substrates for epitaxial growth of diamond[2]. It has the zinc-blend structure (the two-element analogue of diamond), very small lattice mismatch (less than 2%) and a thermal expansion coefficient within 3% that of diamond.

Evidence of epitaxial growth of diamond on c-BN has been previously reported[3-6]. Koizumi et al.[4] found that DC plasma grown diamond showed an epitaxial relationship with the {111} surface of c-BN. The orientation relationship was identified by reflection high-energy electron diffraction (RHEED) as $(111)_{\text{diamond}} // (111)_{\text{c-BN}}$ and $[1\bar{1}0]_{\text{diamond}} // [1\bar{1}0]_{\text{c-BN}}$, i.e., parallel epitaxy. Further support for epitaxial growth of diamond on both {111} and {100} c-BN was obtained from the polarization of the Raman lines[3,5].

Details of the diamond/c-BN interface structure still remain unclear due to a lack of direct observation, e.g., by transmission electron microscopy (TEM). To investigate the interface and to obtain confirmation of parallel epitaxy, we prepared diamond films on several c-BN particles and made cross-sectional TEM characterization of the bicrystal. Electron diffraction, bright-field imaging and high resolution imaging clearly show that the diamond film grew epitaxially on the {111} surface of c-BN with the film and the substrate maintaining a parallel orientation relationship.

Well-shaped cubo-octahedral c-BN crystals (from De Beers Industrial Diamond Division) of about 500 microns in linear dimensions were used as substrates. The diamond films were deposited by hot-filament CVD using 0.5% methane in hydrogen as a source gas at a total pressure of 20 Torr. The temperature of the filament was maintained at 2000°C and the distance between substrate and filament was 5 mm. The temperature of the c-BN particles was estimated to be about 850°C. The detailed experimental procedure is reported elsewhere[7].

Figures 1a) and 1b) show scanning electron micrographs of one of the c-BN particles before and after a 40-hour deposition. The smoothness of the diamond films on some of the c-BN {111} surfaces implies possible epitaxial growth. For cross-sectional TEM sample preparation two c-BN particles with deposited diamond films were epoxied together with the diamond films facing each other. The {111} surfaces of the c-BN particles and their respective $<1\bar{1}0>$ directions were aligned to be parallel with each other. The epoxy was M-bond 610 and the particles were cured for 1.5 hours at 130℃. Since the particles were too small to be clearly seen with bare eyes, the bonding operation was carried out under an enlarging binocular. The characteristic striations[8] of c-BN were used to identify the {001} planes (see the plane indicated by an arrow in Fig. 1a) and its edges were used to identify the <110> directions. Based on the surface morphology reported by Mishima[8], we believe that the (111) labeled c-BN surface shown in Fig. 1a) and the interface shown in Fig. 2 are boron-terminated. After the sandwiched particles were cured, they were put into a 2 mm brass tube in order to make a disk sample. The tube was filled with an alumina slurry (Ceramabond 503) and placed in an oven for programmed curing up to 370°C. Care was taken that the $[1\bar{1}0]$ direction of the c-BN particles, i.e., the viewing direction, was kept aligned with the axis of the brass tube.

After curing, the disk sample was polished on a diamond abrasive plate to a thickness of about 100 μm. Then it was carefully broken and the sandwiched particles were removed from the slurry and bonded to a home-made molybdenum grid using 5-minute epoxy. The sample was further thinned by dimpling to 30-40 μm, followed by ion beam milling. Although c-BN has a hardness comparable to that of diamond, the difference in sputtering rate between them is still quite significant. Consequently, two metal obstacles were placed on the specimen holder in order to protect the interface during ion milling.

Figure 2(a) shows the morphology of the diamond/c-BN interface. The thickness of the diamond layer is more than 10 μm and most of the c-BN has been sputtered away. The bright-field image of the interface (Fig.2a) shows that the diamond film contains numerous twins. The high resolution micrograph viewed along $[1\bar{1}0]$ (Fig. 2b) gives a more detailed atomic view of the interface. The clean interface is particularly interesting because the films were grown by hot-filament deposition. No evidence of tungsten, tungsten carbide or other phases was observed at the interface. A misfit dislocation at the diamond/c-BN interface is arrowed in Fig. 2b). The region containing this dislocation is shown at a higher magnification in Fig. 2c). From the Burgers circuit in this figure the projection of the Burgers vector along the viewing direction is $a/4[11\bar{2}]$. It is then possible that the total Burgers vector of the misfit dislocation is $a/2[01\bar{1}]$, inclined at 60° with respect to the incident beam. An array of misfit dislocations with this Burgers vector is expected to occur at a spacing of about 15 nm, although the spacing was observed to be not very regular in the present specimen.

Figure 3 shows the $[1\bar{1}0]$ zone axis electron diffraction patterns taken from (a) the diamond film, (b) the c-BN substrate, and (c) the interface. These almost identical diffraction patterns indicate a perfect parallel orientation relationship between the diamond film and its substrate: $(111)_{diamond}$ // $(111)_{c\text{-}BN}$ and $[1\bar{1}0]_{diamond}$ // $[1\bar{1}0]_{c\text{-}BN}$. To avoid ambiguity in distinguishing diamond from c-BN, both <110> and <100> zone axis diffraction patterns were taken. The absence of {002} diffraction spots is a well-known characteristic of the diamond structure. They are kinematically forbidden, but can be dynamically excited by double diffraction when viewed along a <110> direction. For this reason, no difference can be observed between the diffraction patterns of diamond and c-BN in this direction. On the other hand, when diamond is viewed along a <100> direction, the {002} spots are dynamically extinguished, while those of c-BN appear both kinematically and dynamically due to the difference in scattering factors between boron and nitrogen. Figure 4 shows the <100> diffraction patterns taken from (a) the diamond and (b) the c-BN substrate. The absence and presence, respectively, of {002} diffraction spots is clearly shown in Figs. 4a and 4b, which provides a criterion for determining the diamond side, the c-BN side and the position of the interface without ambiguity.

In conclusion, it is found that diamond can be grown with parallel epitaxy on the {111} surface of c-BN by hot-filament chemical vapor deposition. The parallel orientation relationship has been confirmed by electron diffraction and HREM. The interface was found to be clean and free of any other phases.

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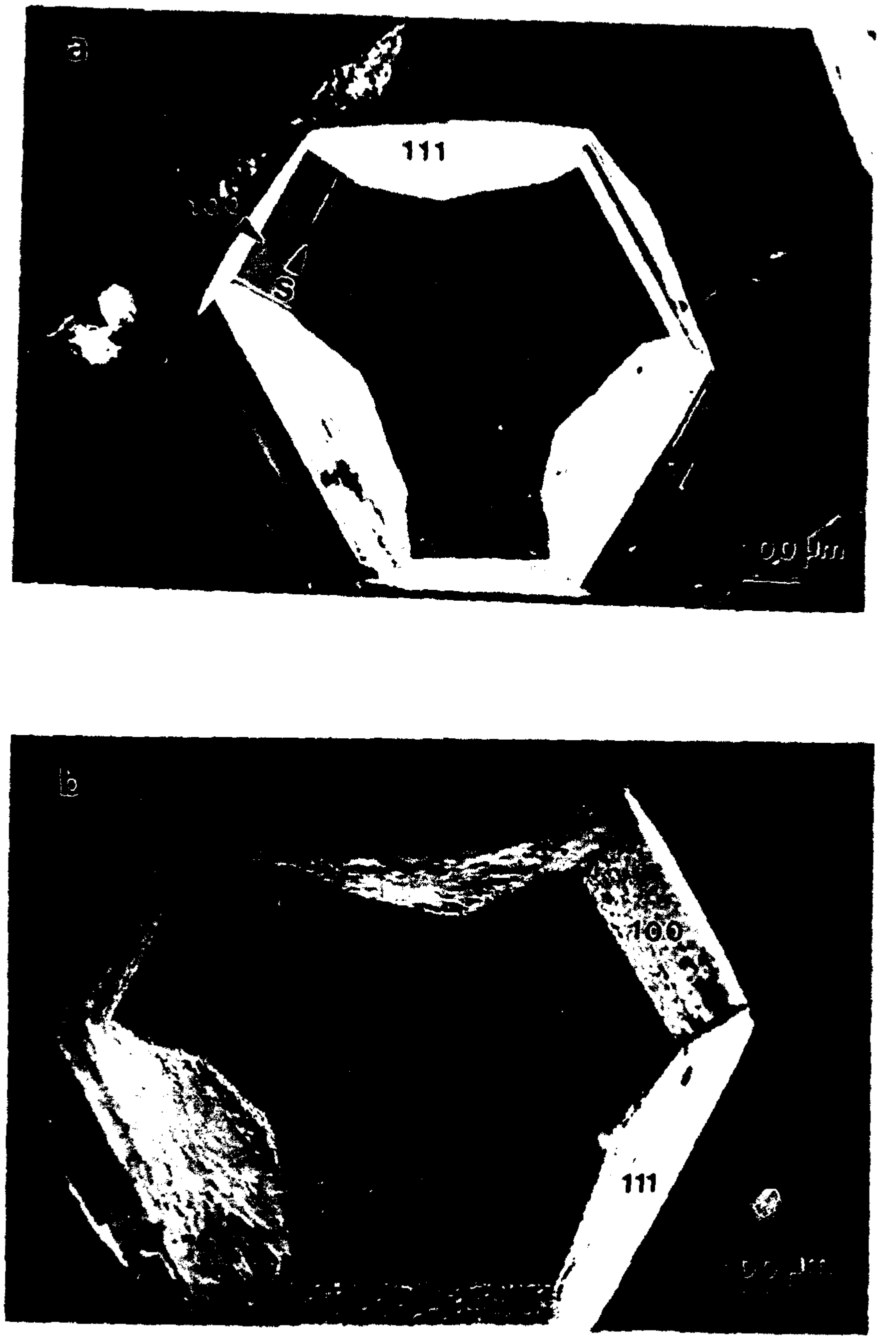

Figure 1. SEM micrograph of a c-BN particle (a) before and (b) after deposition. The arrow in (a) indicates a {100} plane with characteristic striations.

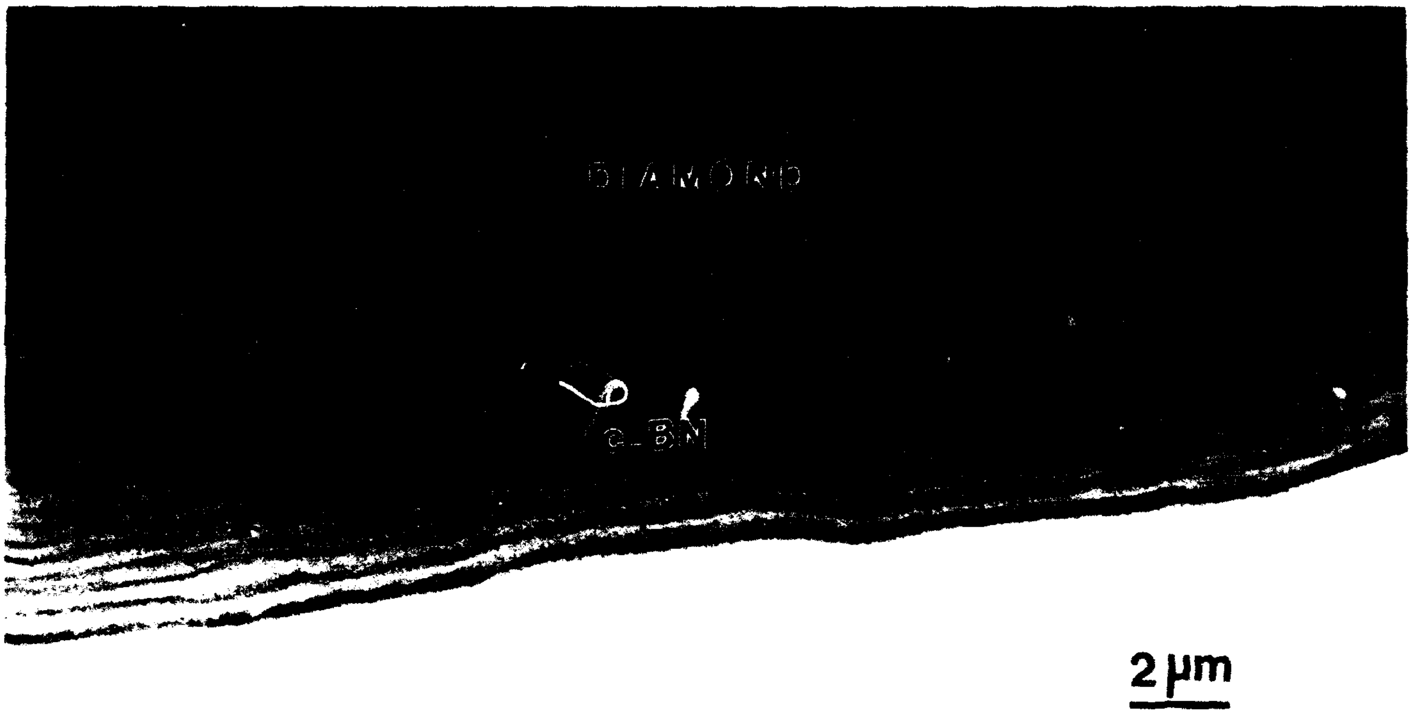

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Figure 2a. Bright-field TEM micrograph of the deposited diamond film on a c-BN substrate.

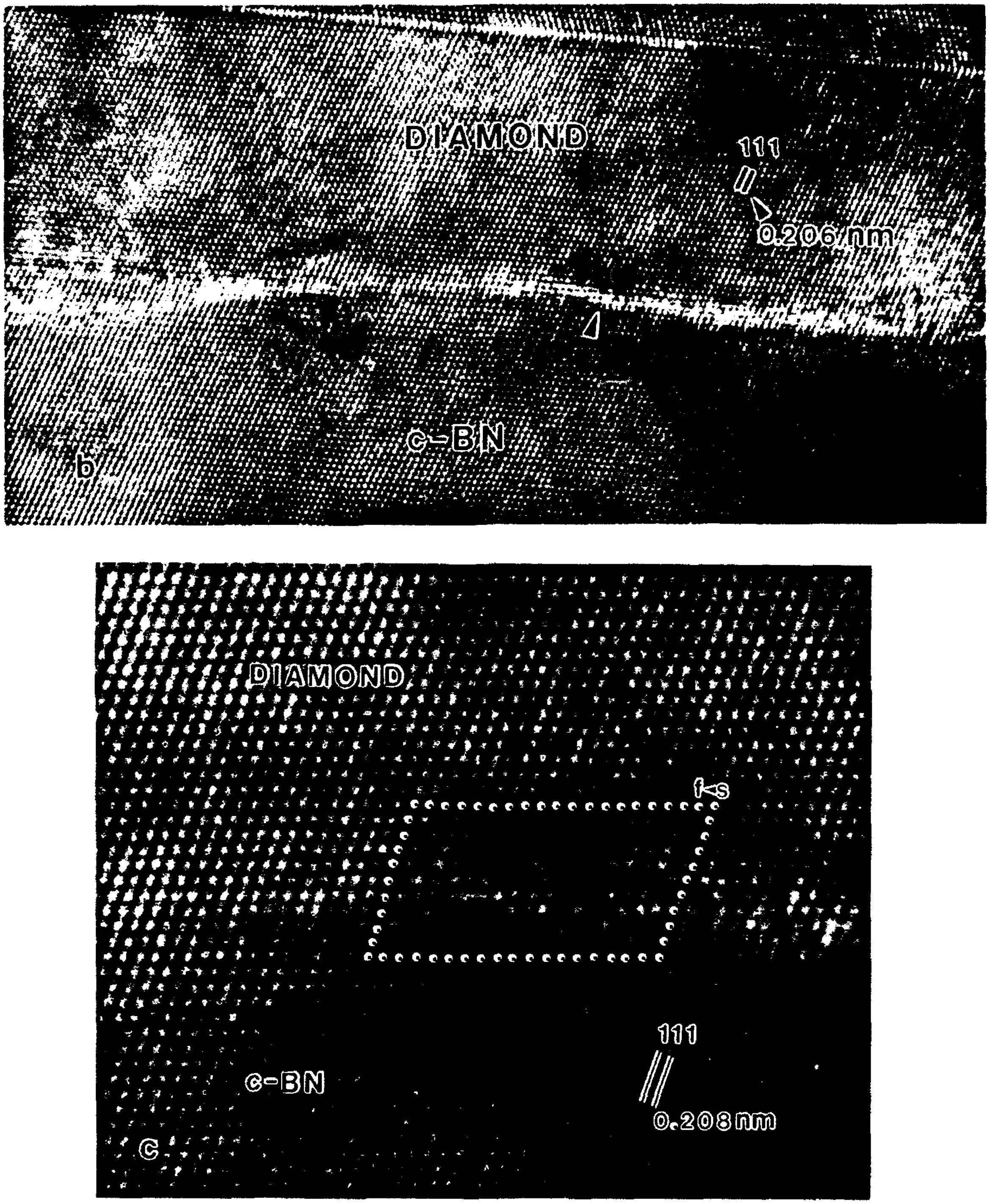
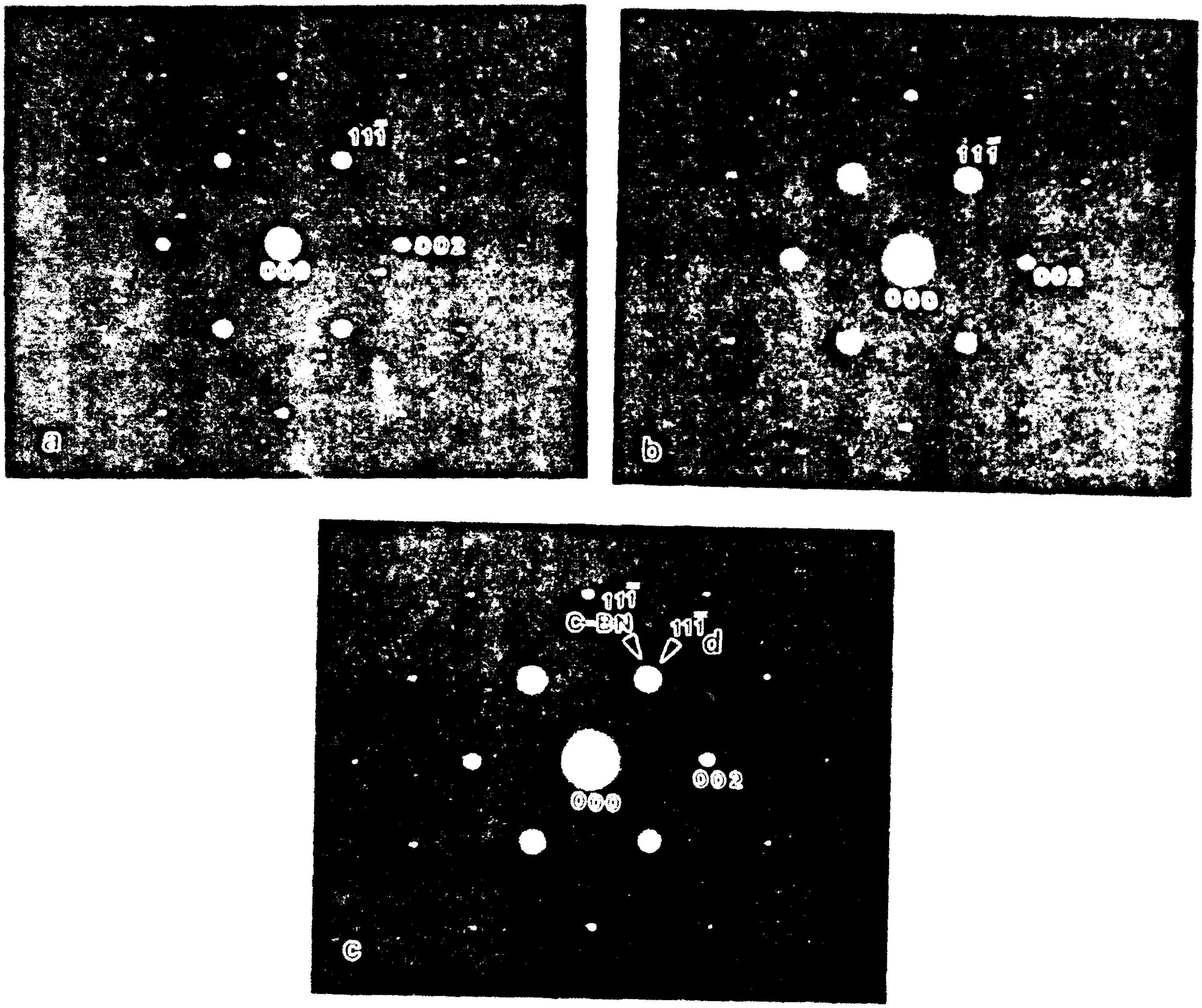


Figure 2. TEM micrograph of the deposited diamond film on a c-BN substrate: (b) High-resolution micrograph; the arrow indicates a misfit dislocation, (c) Enlargement of the region containing the misfit dislocation.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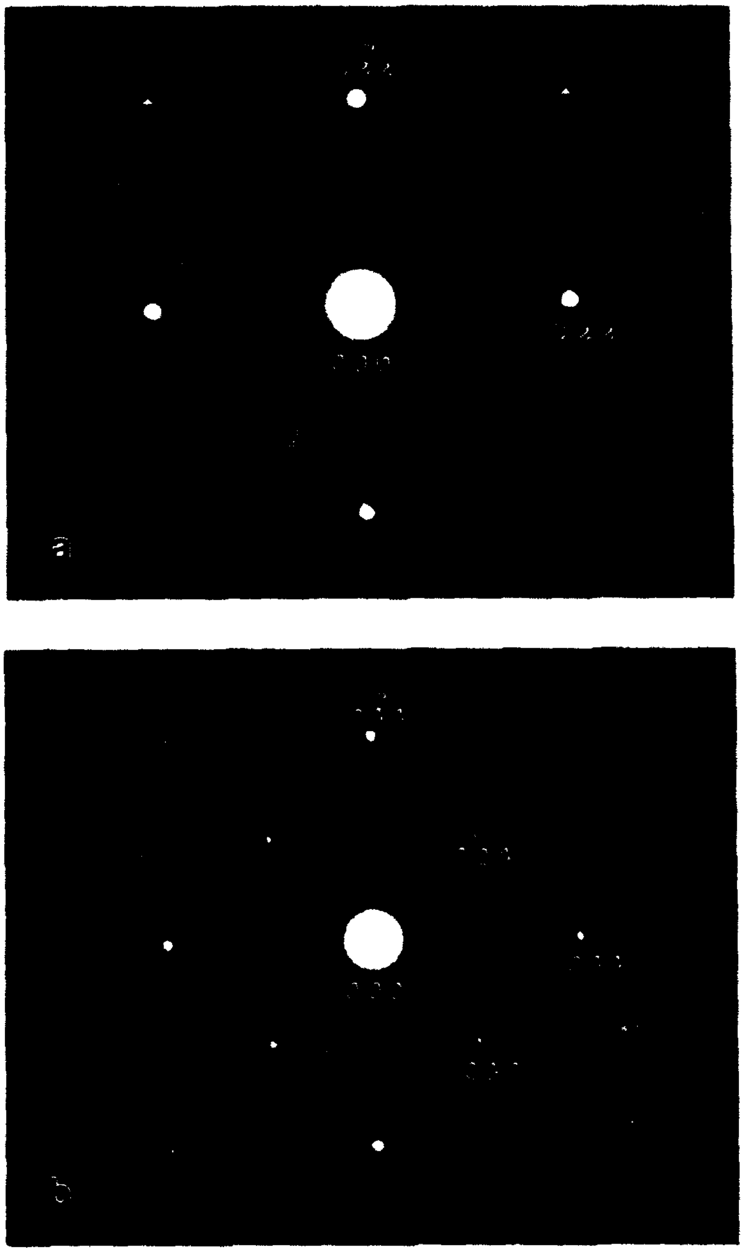

Figure 4. <100> zone axis electron diffraction pattern taken from (a) the diamond film and (b) the c-BN substrate.